

Synthesis of luminescent ceramics from alumina nanopowder

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Abstract. The effect of the conditions of high-temperature synthesis in a reducing medium on the density, area and cathodoluminescence of ceramics made of compacted $\alpha\text{-Al}_2\text{O}_3$ powder is the focus of this work. The dependence of the luminescence intensity on the temperature and duration of the synthesis of ceramics is presented. The optimal parameters for synthesis of luminescent ceramics from alumina nanopowder are defined.

1. Introduction

Alumina is a well-known functional material which has a wide range of practical applications. One of them is related to using oxygen-deficient single crystals and microcrystalline powders as dosimetric phosphors [1, 2]. High sensitivity of oxygen-deficient oxides to ionizing radiation is caused by vacancies in the anion sublattice. While the vacancies capture one or two electrons, they create F^+ and F-centers. Such centers are involved in the process of luminescence. The most effective method of formation of F and F^+ centers is growing single crystals from melting (Stepanov's method) in a highly reducing medium in the presence of carbon with a low partial pressure of oxygen. In this case an increasing temperature in crystal growing chamber leads to the formation of carbon monoxide (CO) which is a strong reducing agent and facilitates oxygen vacancy creation in the oxide.

Nowadays using nanopowders of various compounds as phosphors is proved to be promising. Ceramics with high mechanical durability are considered to be the most suitable materials for technological applications. Ceramics are useful for production of luminescent detectors and sensors of any shape and size. The existing methods allow us to obtain alumina nanopowders with a stoichiometric structure. To produce luminescent ceramics it is necessary to carry out their synthesis in reducing medium. Oxygen-deficient ceramics synthesis from alumina nanopowder has been little studied. A research of the effect of synthesis conditions on ceramic luminescent properties is required.

The aim of this paper is to study the processes of the ceramics synthesis from alumina nanopowders in a reducing medium and to define the influence of the synthesis conditions on its luminescence excited by means of a pulse electron beam.

2. Samples and methods

High purity $\alpha\text{-Al}_2\text{O}_3$ powder (99.9%) with the particle size of 50-70 nm was used for the production of samples. The compacts were prepared by using cold uniaxial pressing in the hydraulic press Specac at a pressure of 1000 kgf/cm². The compacts 5 mm in diameter and 1.3 mm thick had the mass of 40 mg and the density of 1.56 g/cm³. A high-temperature vacuum electric furnace was used to synthesize ceramics. The electric furnace allows the sample to be annealed at temperatures up to 1800°C and in vacuum of about 10⁻² Pa. The synthesis of ceramics was carried out in the presence of graphite rods (20 g).



Pulse cathodoluminescence (PCL) of the ceramics was measured by an analyzer "CLAVI". Luminescence excitation was induced in the samples with an electron beam while they were irradiated in the air at room temperature. The duration of the beam was 2 ns, the maximum electrons energy was about 130 ± 10 keV, the current density was 60 A/cm². The spectral range of PCL measurements was 350-750 nm. The wavelength measurement inaccuracy was $\lambda = \delta \pm 0.75$ nm.

3. Results and discussion

3.1. The synthesis of ceramics under different conditions

The area of the samples synthesized at 900 – 1600°C for 60 minutes either in the presence of carbon or without it significantly changes. This effect can be explained by the ceramics sintering processes (Figure 1a). The sintering causes porosity decrease and nanoparticles agglomeration [3]. The area change of the samples sintered at above 1500°C without graphite is slowed down, which is caused by the sintering completion. In the samples annealed in the carbon presence at the temperatures over 1500°C the further area decrease leads to its evaporation.

It is known from the published data that high-temperature heating (more than 1500°C) in a vacuum causes thermal etching [4, 5]. It leads to decreasing mass of the sample. One can assume that in the presence of carbon a thermal etching is intensified due to the loss of oxygen in the oxide reduction. As a result, Al₂O₃ breaks down into lower oxides which are to be deleted during pumping. It means that the temperature of 1500°C is ultimate for the synthesis of oxygen-deficient alumina ceramics in a highly reducing medium.

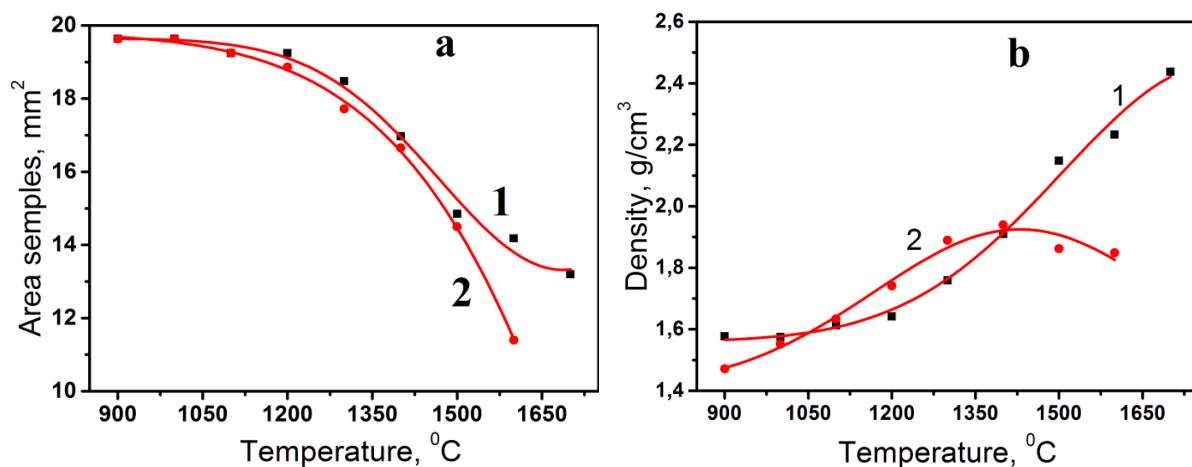


Figure 1. Dependences of the changes in the area (a) and density (b) of Al₂O₃ ceramics on the synthesis temperatures: 1-without carbon, 2-with carbon.

To calculate the density of the samples, their mass, diameter and height were measured. Figure 1b shows that the temperature increase causes the density growth in the samples either annealed in vacuum or synthesized in the presence of carbon. In the latter case the density growth is replaced by the saturation and even by a decrease in its value in the temperature range of 1400-1500°C. This result correlates with the mentioned above temperature influence on the sample area, i.e. the result is caused by a loss of the sample mass during its intensive thermal etching and subsequent decomposition into lower aluminum oxides.

3.2. Pulse cathodoluminescence

Spectra of PCL were measured in order to define the ceramics synthesis conditions which lead to creation of highest concentration of oxygen vacancies. Such vacancies are luminescence centers. The PCL of ceramics synthesis in a vacuum in the presence of carbon were measured at different

temperatures. It is known that F-centers created by oxygen vacancies are responsible for the emission band with the maximum at 420nm [5]. Observation of the changes in the intensity of this band at various temperatures of the ceramics synthesis shows relative changes of oxygen vacancies concentration. The results of the measurements of the PCL band intensity were obtained taking into account the change in the sample area after synthesis.

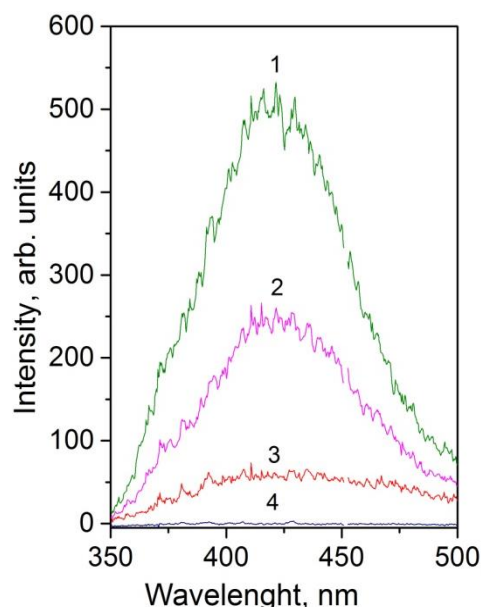


Figure 2. PCL spectra of ceramics synthesized in presence of carbon for 1 h at different temperatures: 1 – 1600°C, 2 – 1500°C, 3 – 1300°C; 4 – without carbon at T=1600°C.

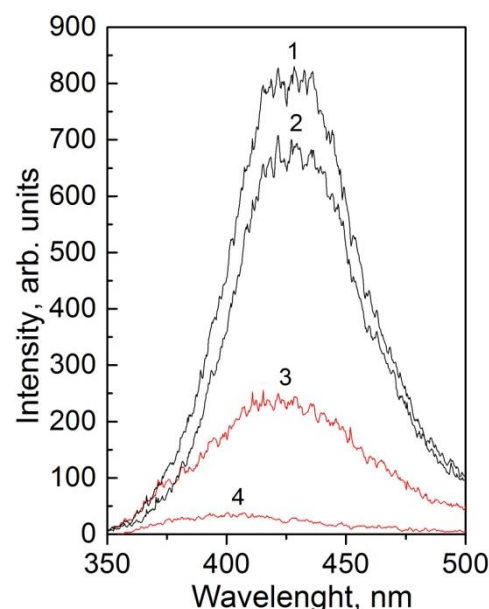


Figure 3. PCL spectra of ceramics synthesized at various durations of sintering: 1 – 300 min, 2 – 180 min, 3 – 60 min; 4 – without carbon for 300 min.

One can see that an increasing synthesis temperature leads to the intensity growth of the PCL emission band at 420 nm (Figure 2). The most significant PCL intensity growth occurs between 1300 and 1500°C. It should be noted that ceramics synthesis in vacuum without carbon is of low efficiency for creation of oxygen vacancies.

To define an effect of the annealing time on the PCL intensity, the period of isothermal heating was changed in the samples annealed in the presence of carbon at 1500°C (60 min, 180 min and 300 min.). The PCL spectra of these samples are shown in Figure 3. An increasing annealing time of alumina ceramics synthesis in a reducing medium also leads to luminescence intensity growth at the 420 nm band. The luminescence increase indicates anion defects and a growth of luminescence centers concentration in the oxygen sublattice of the oxide. A slight difference of the PCL intensities of the samples with a synthesis time of 180 and 300 min should be noted.

The experiments carried out allowed us to define the optimal parameters for synthesis of luminescent ceramics from alumina nanopowder, which give quite a high PCL yield with a relatively small loss of the sample mass. The temperature of 1500°C can be recommended for annealing for less than 3 hours.

4. Conclusion

1. Oxygen-deficient alumina ceramics have been synthesized under different temperatures in vacuum in the presence of carbon. It has been shown that the samples lose mass due to thermal etching at temperatures above 1500°C.
2. PCL spectra of ceramics synthesized at high-temperature in a strongly reducing environment have a band centered at 420 nm resulted from luminescence of F centers.

3. The increase in synthesis temperature up to 1500°C and annealing time up to 3 hours lead to the luminescence intensity growth in the samples without any substantial destruction of the samples due to thermal etching.
4. The obtained ceramics can be used to assess the possibilities of creation the luminescent detectors of ionizing radiation on their base and for other technical applications, in particular, in plasma display panels and optoelectronic devices.

5. Acknowledgments

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6. References

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